

Manufactured Solution for 1D Transient Euler Equations for Hypersonic Flows with Nitrogen Dissociation in Thermal Nonequilibrium*

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Abstract

The Method of Manufactured Solutions is a valuable approach for code verification, providing means to verify how accurately the numerical method solves the equations of interest. The method generates a related set of governing equations that has known analytical (manufactured) solution. Then, the modified set of equations may be discretized and solved numerically, and the numerical solution may be compared to the manufactured analytical solution chosen *a priori*.

A choice of analytical solutions for the flow variables of the 1D transient Euler equations for chemically reacting hypersonic flows in thermal nonequilibrium and their respective source terms are presented in this document.

1 Mathematical Model

Using the two-temperature model, the conservation of mass, momentum, and energy for a inviscid compressible fluid composed of a mixture of gases N and N₂ in thermochemical nonequilibrium may be written

*Work based on Kirk, Amar, Stogner, Schultz, and Oliver (2009).

as:

$$\frac{\partial \rho_N}{\partial t} + \nabla \cdot (\rho_N \mathbf{u}) = \dot{\omega}_N, \quad (1)$$

$$\frac{\partial \rho_{N_2}}{\partial t} + \nabla \cdot (\rho_{N_2} \mathbf{u}) = \dot{\omega}_{N_2}, \quad (2)$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p, \quad (3)$$

$$\frac{\partial \rho E}{\partial t} + \nabla \cdot (\rho \mathbf{u} H) = 0, \quad (4)$$

$$\frac{\partial \rho e_V}{\partial t} + \nabla \cdot (\rho e_V \mathbf{u}) = \dot{\omega}_V, \quad (5)$$

where ρ_s is the density of species s (N or N_2), $\rho = \sum_s \rho_s$ is the mixture density, \mathbf{u} is the mixture velocity and e_V is the vibrational/electronic energy. The total enthalpy, H , may be expressed in terms of the total energy, density, and pressure:

$$H = E + \frac{p}{\rho},$$

where the total energy, E , is composed of internal and kinetic components:

$$E = e^{\text{int}} + \frac{u^2}{2}.$$

The total internal energy, e^{int} , has contributions from each of the distinct energy *modes*:

$$\begin{aligned} e^{\text{int}} &= e^{\text{trans}} + e^{\text{rot}} + e^{\text{vib}} + e^{\text{elec}} + h^0 \\ &= \sum_{s=1}^{ns} c_s e_s^{\text{trans}} + \sum_{s=\text{mol}} c_s e_s^{\text{rot}} + \sum_{s=\text{mol}} c_s e_s^{\text{vib}} + \sum_{s=1}^{ns} c_s e_s^{\text{elec}} + \sum_{s=1}^{ns} c_s h_s^0, \end{aligned} \quad (6)$$

where $c_s = (\rho_s/\rho)$ is the mass fraction of species s .

The first four terms on the right of Equation (6) represent the energy due to molecular/atomic translation, molecular rotation, molecular vibration, and electronic excitation. The final term is the heat of formation of the mixture and accounts for the energy stored in chemical bonds (Ait-Ali-Yahia, 1996; Kirk et al., 2009). In the two-temperature model, the translational and rotational modes may modeled with a single translational/rotational temperature $T \equiv T_t = T_r$, while the vibrational and electronic energy are governed by a separate temperature $T_V \equiv T_v = T_e$.

Under the approximation that the translational and rotational states of the may be assumed fully populated, translational/rotational energy for each species may be expressed as:

$$e_s^{\text{trans}} + e_s^{\text{rot}} = e_s^{\text{tr}} = C_{v,s}^{\text{tr}} T, \quad (7)$$

where the translational/rotational specific heat, $C_{v,s}^{\text{tr}}$ is given by

$$C_{v,s}^{\text{tr}} = \begin{cases} \frac{5}{2} R_s & \text{for molecules,} \\ \frac{3}{2} R_s & \text{for atoms,} \end{cases}$$

where R_s is the species gas constant, and $R_s = R/M_s$ where R is the universal gas constant and M_s is the species molar mass. The combined term e_s^{tr} in Equation (7) represents the energy due to random thermal translational/rotational motion of a given species.

In contrast to the translational/rotational states, the vibrational energy states are typically not fully populated. One approach for modeling the molecular vibrational energy is through analogy to a harmonic oscillator. In this approach the energy potential between molecular nuclei is modeled as a quadratic function of separation distance. Under this assumption, the vibrational energy for each molecular species can be modeled as:

$$e_s^{\text{vib}} = \begin{cases} \frac{R_s \theta_s^{\text{vib}}}{\exp(\theta_s^{\text{vib}}/T_v) - 1} & \text{for molecules,} \\ 0 & \text{for atoms,} \end{cases} \quad (8)$$

where θ_s^{vib} is the species characteristic temperature of vibration and T_v is the mixture vibrational temperature.

The energy contained in the excited electronic states for a given species, e_s^{elec} , can be obtained from the assumption that they are in a Boltzmann distribution governed by the electronic excitation temperature T_e (Candler, 1988) as:

$$e_s^{\text{elec}} = R_s \frac{\sum_{i=1}^{\infty} \theta_{s,i}^{\text{elec}} g_{s,i} \exp(-\theta_{s,i}^{\text{elec}}/T_e)}{\sum_{i=1}^{\infty} g_{s,i} \exp(-\theta_{s,i}^{\text{elec}}/T_e)}. \quad (9)$$

where $g_{s,i}$ is the degeneracy of the electronic level i of species s , and $\theta_{s,i}^{\text{elec}}$ is its characteristic temperature. In practice, a simple cut off criteria is applied to select the number of electronic energy levels in the calculation of the series.

Recalling that in the two-temperature mode adopted in this work $T_e = T_v = T_V$, Equations (8) and (9) may be simplified to:

$$e_s^{\text{vib}} = \begin{cases} \frac{R_s \theta_s^{\text{vib}}}{\exp(\theta_s^{\text{vib}}/T_V) - 1} & \text{for molecules,} \\ 0 & \text{for atoms,} \end{cases} \quad e_s^{\text{elec}} = R_s \frac{\sum_{i=1}^{nel_s} \theta_{s,i}^{\text{elec}} g_{s,i} \exp(-\theta_{s,i}^{\text{elec}}/T_V)}{\sum_{i=1}^{nel_s} g_{s,i} \exp(-\theta_{s,i}^{\text{elec}}/T_V)}.$$

where nel_s is the number of electronic energy levels of species s . See Appendix A for N and N₂ data.

Therefore,

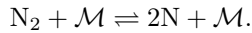
$$\rho e_V(T_V) = \sum_{s=\text{mol}}^{ns} \rho_s e_s^{\text{vib}}(T_V) + \sum_{s=1}^{ns} \rho_s e_s^{\text{elec}}(T_V). \quad (10)$$

Regardless of the thermal state of the mixture, once the translational/rotational temperature T is determined the thermodynamic pressure of the mixture is readily obtained from Dalton's law of partial pressures:

$$p = \sum_{s=1}^{ns} p_s = \sum_{s=1}^{ns} \rho_s R_s T. \quad (11)$$

1.1 Chemical Kinetics

The rate of production/destruction of the individual species s , $\dot{\omega}_s$, is required to close the species continuity equations. For the dissociating Nitrogen flow ($\text{N}_2 \rightleftharpoons 2\text{N}$) case, let us consider the chemical reactions which occur among the five principal components of dissociating air – N₂, O₂, NO, N, O – but neglecting three species in order to perform this 2-species problem. For this mixture, the single chemical reaction that occur is:



This reaction can occur in either the forward or backward direction, as denoted by the bidirectional arrow. The reaction is presented such that they are endothermic in the forward direction, and \mathcal{M} denotes a generic collision partner, which may be any of the species present in the flow, and is unaltered by the reaction (Kirk et al., 2009). The rate of each reaction is therefore a sum of the forward and backward rates, k_f and k_b :

$$\begin{aligned} \mathcal{R}_r &= \mathcal{R}_{br} - \mathcal{R}_{fr} \\ &= k_{br} \prod_{s=1}^{ns} \left(\frac{\rho_s}{M_s} \right)^{\beta_{sr}} - k_{fr} \prod_{s=1}^{ns} \left(\frac{\rho_s}{M_s} \right)^{\alpha_{sr}} \end{aligned}$$

where α_{sr} and β_{sr} are the stoichiometric coefficients for reactants and products of species s . For the Nitrogen dissociation,

$$\begin{aligned} \mathcal{R}_1 &= \sum_{m \in \mathcal{M}} \left(k_{b_1 m} \frac{\rho_N}{M_N} \frac{\rho_N}{M_N} \frac{\rho_m}{M_m} - k_{f_1 m} \frac{\rho_{\text{N}_2}}{M_{\text{N}_2}} \frac{\rho_m}{M_m} \right) \\ &= k_{b_1 \text{N}} \frac{\rho_{\text{N}}^3}{M_{\text{N}}^3} - k_{f_1 \text{N}} \frac{\rho_{\text{N}_2} \rho_{\text{N}}}{2 M_{\text{N}}^2} + k_{b_1 \text{N}_2} \frac{\rho_{\text{N}}^2 \rho_{\text{N}_2}}{2 M_{\text{N}}^3} - k_{f_1 \text{N}_2} \frac{\rho_{\text{N}_2}^2}{4 M_{\text{N}}^2}, \end{aligned} \quad (12)$$

recalling that $M_{\text{N}_2} = 2M_{\text{N}}$.

The species source terms $\dot{\omega}_s = M_s \sum_{r=1}^{nr} (\alpha_{sr} - \beta_{sr}) (\mathcal{R}_{br} - \mathcal{R}_{fr})$ where nr is the number of reactions can now be expressed in terms of the individual reaction rates as follows:

$$\begin{aligned}\dot{\omega}_{N_2} &= M_{N_2} (\mathcal{R}_1) = 2M_N \mathcal{R}_1, \\ \dot{\omega}_N &= M_N (-2\mathcal{R}_1) = -2M_N \mathcal{R}_1.\end{aligned}$$

Note that these source terms sum identically to zero, as required by conservation of mass (Kessler and Awruch, 2004).

The forward rate coefficients k_{fr} can then be expressed in a modified Arrhenius form as

$$k_{fr}(\bar{T}) = C_{fr} \bar{T}^{\eta_r} \exp(-E_{ar}/R\bar{T}) \quad (13)$$

where C_{fr} is the reaction rate constant, η_r is the so-called pre-exponential factor, E_{ar} is the activation energy. These three constants are determined from curve fits to experimental data (e.g. see Ait-Ali-Yahia (1996)). The effective temperature, \bar{T} , is a function of the translational/rotational and vibrational temperatures, and in this work it is taken as:

$$\bar{T} = T^q T_V^{1-q}, \quad 0 \leq q \leq 1. \quad (14)$$

The corresponding backward rate coefficient k_{br} can be found using the principle of detailed balance, which states

$$K_{eq} = \frac{k_{fr}(\bar{T})}{k_{br}(\bar{T})} \quad (15)$$

where K_{eq} is the equilibrium constant and may be obtained either by curve fits or through Gibbs' free energy techniques¹. In this work, $K_{eq} = K(T)$. Therefore:

$$\begin{aligned}k_{f_1N} &= C_{f_1N} \bar{T}^{\eta_{f_1N}} \exp\left(\frac{-E_{aN}}{R\bar{T}}\right) \quad \text{and} \quad k_{b_1N} = \frac{k_{f_1N}}{K(T)}, \\ k_{f_1N_2} &= C_{f_1N_2} \bar{T}^{\eta_{f_1N_2}} \exp\left(\frac{-E_{aN_2}}{R\bar{T}}\right) \quad \text{and} \quad k_{b_1N_2} = \frac{k_{f_1N_2}}{K(T)},\end{aligned} \quad (16)$$

are the forward and backward rates for Nitrogen atom and Nitrogen molecule, respectively.

1.2 Vibrational/Electronic Energy Production & Vibrational Relaxation

For the case of thermal nonequilibrium it remains to define the vibrational/electronic energy source term, $\dot{\omega}_v$, which appears in Equation (5). This term represents the production/destruction of vibrational/electronic energy in the gas, and is due to both the creation of molecules with some vibrational/electronic energy and the transfer of energy between the various modes in the gas:

$$\dot{\omega}_v = \dot{Q}_v + \dot{Q}_{\text{transfer}}.$$

When molecular species are created in the gas at rate $\dot{\omega}_s$, they contribute vibrational/electronic energy at the rate:

$$\dot{Q}_{vs} = \dot{\omega}_s (e_s^{\text{vib}} + e_s^{\text{elec}}),$$

so the net vibrational energy production rate is then simply:

$$\dot{Q}_v = \sum_{s=1}^{ns} \dot{\omega}_s (e_s^{\text{vib}} + e_s^{\text{elec}}). \quad (17)$$

There is also energy transfer among the various energy modes in the gas. Strictly speaking, one such energy transfer is vibration-vibration coupling between the various molecules in the gas. However, implicit in the use of a single vibrational energy equation is the assumption that the molecular vibrational energies equilibrate very rapidly and thus are adequately characterized with a single vibrational temperature T_V . There is also

¹Examples of curve fits for calculating the equilibrium constant may be found in Park (1990), whereas Gibbs' free energy techniques are employed in McBride et al. (2002).

energy transfer between translational and vibrational modes as well as rotational and vibrational modes (Kirk et al., 2009). These latter two exchanges are grouped together and represented as a single vibrational energy transfer rate $\dot{Q}^{\text{tr-vib}}$. In this work we adopt the Landau-Teller model for the vibrational energy transfer for a given species:

$$\dot{Q}_s^{\text{tr-vib}} = \rho_s \frac{\hat{e}_s^{\text{vib}} - e_s^{\text{vib}}}{\tau_s^{\text{vib}}}, \quad (18)$$

where \hat{e}_s^{vib} is the species equilibrium vibrational energy (Equation (8) evaluated at temperature T) and the vibrational relaxation time τ_s^{vib} is given by:

$$\tau_s^{\text{vib}} = \frac{\sum_{r=1}^{ns} \chi_r}{\sum_{r=1}^{ns} \chi_r / \tau_{sr}^{\text{vib}}}$$

where:

$$\begin{aligned} \chi_r &= c_r \frac{M}{M_r}, \quad \text{with} \quad M = \left(\sum_{s=1}^{ns} \frac{c_s}{M_s} \right)^{-1}, \\ \tau_{sr}^{\text{vib}} &= \frac{1}{P} \exp \left[A_{sr} \left(T^{-1/3} - 0.015 \mu_{sr}^{1/4} \right) - 18.42 \right], \\ A_{sr} &= 1.16 \times 10^{-3} \mu_{sr}^{1/2} (\theta_s^{\text{vib}})^{4/3}, \\ \mu_{sr} &= \frac{M_s M_r}{M_s + M_r}. \end{aligned}$$

Combining (17) and (18) yields the desired net vibrational energy source term:

$$\dot{\omega}_V = \sum_{s=1}^{ns} \dot{Q}_s^{\text{tr-vib}} + \sum_{s=1}^{ns} \dot{\omega}_s (e_s^{\text{vib}} + e_s^{\text{elec}}).$$

2 Manufactured Solutions

Roy et al. (2002) introduce the general form of the primitive manufactured solution variables to be a function of sines and cosines in x , y and z only. In this work, Roy et al. (2002)'s manufactured solutions are modified in order to address temporal accuracy as well:

$$\phi(x, t) = \phi_0 + \phi_x f_s \left(\frac{a_{\phi x} \pi x}{L} \right) + \phi_t f_s \left(\frac{a_{\phi t} \pi t}{L} \right), \quad (19)$$

where $\phi = \rho_N, \rho_{N_2}, u, T$ or T_V , and $f_s(\cdot)$ functions denote either sine or cosine function. Note that in this case, ϕ_x is constant and the subscript does not denote differentiation. Different choices of the constants used in the manufactured solutions for the 2D supersonic and subsonic cases of Euler and Navier-Stokes may be found in Roy et al. (2002).

Therefore, the manufactured analytical solution for each one of the variables in Euler equations are:

$$\begin{aligned} \rho_N(x, t) &= \rho_{N0} + \rho_{Nx} \sin \left(\frac{a_{\rho Nx} \pi x}{L} \right) + \rho_{Nt} \cos \left(\frac{a_{\rho Nt} \pi t}{L} \right), \\ \rho_{N_2}(x, t) &= \rho_{N_20} + \rho_{N_2x} \cos \left(\frac{a_{\rho N_2x} \pi x}{L} \right) + \rho_{N_2t} \sin \left(\frac{a_{\rho N_2t} \pi t}{L} \right), \\ u(x, t) &= u_0 + u_x \sin \left(\frac{a_{ux} \pi x}{L} \right) + u_t \cos \left(\frac{a_{ut} \pi t}{L} \right), \\ T(x, t) &= T_0 + T_x \cos \left(\frac{a_{Tx} \pi x}{L} \right) + T_t \cos \left(\frac{a_{Tt} \pi t}{L} \right), \\ T_V(x, t) &= T_{V0} + T_{Vx} \cos \left(\frac{a_{T_Vx} \pi x}{L} \right) + T_{Vt} \sin \left(\frac{a_{T_Vt} \pi t}{L} \right), \end{aligned} \quad (20)$$

Recalling that $\rho = \sum_s \rho_s$, the manufactured analytical solution for the density of the mixture is:

$$\rho(x, t) = \rho_N(x, t) + \rho_{N_2}(x, t). \quad (21)$$

2.1 1D Transient Euler Equations in Thermochemical Nonequilibrium

The MMS applied to 1D transient Euler equations for a chemically reacting mixture of N and N₂ in thermal nonequilibrium consists in modifying Equations (1)–(5) by adding a source term to the right-hand side of each equation:

$$\begin{aligned}
\frac{\partial(\rho_N)}{\partial t} + \frac{\partial(\rho_N u)}{\partial x} - \dot{\omega}_N &= Q_{\rho_N}, \\
\frac{\partial(\rho_{N_2})}{\partial t} + \frac{\partial(\rho_{N_2} u)}{\partial x} - \dot{\omega}_{N_2} &= Q_{\rho_{N_2}}, \\
\frac{\partial(\rho u)}{\partial t} + \frac{\partial(\rho u^2)}{\partial x} + \frac{\partial(p)}{\partial x} &= Q_u, \\
\frac{\partial(\rho E)}{\partial t} + \frac{\partial(\rho u E)}{\partial x} + \frac{\partial(pu)}{\partial x} &= Q_E, \\
\frac{\partial(\rho e_V)}{\partial t} + \frac{\partial(\rho e_V u)}{\partial x} - \dot{\omega}_V &= Q_{e_V},
\end{aligned} \tag{22}$$

so the modified set of Equations (22) conveniently has the analytical solutions given in Equations (20) and (21).

Source terms Q_{ρ_N} , $Q_{\rho_{N_2}}$, Q_u , Q_E and Q_{e_V} are obtained by symbolic manipulations of equations above using Maple and are presented in the following sections. The following auxiliary variables have been included in order to improve readability and computational efficiency:

$$\begin{aligned}
\text{Rho}_N &= \rho_{N0} + \rho_{Nx} \sin\left(\frac{a_{Nx}\pi x}{L}\right) + \rho_{Nt} \cos\left(\frac{a_{Nt}\pi t}{L}\right), \\
\text{Rho}_{N_2} &= \rho_{N_20} + \rho_{N_2x} \cos\left(\frac{a_{N_2x}\pi x}{L}\right) + \rho_{N_2t} \sin\left(\frac{a_{N_2t}\pi t}{L}\right), \\
\text{Rho} &= \text{Rho}_N + \text{Rho}_{N_2}, \\
U &= u_0 + u_x \sin\left(\frac{a_{ux}\pi x}{L}\right) + u_t \cos\left(\frac{a_{ut}\pi t}{L}\right), \\
T &= T_0 + T_x \cos\left(\frac{a_{Tx}\pi x}{L}\right) + T_t \cos\left(\frac{a_{Tt}\pi t}{L}\right), \\
T_V &= T_{V0} + T_{Vx} \cos\left(\frac{a_{Vx}\pi x}{L}\right) + T_{Vt} \sin\left(\frac{a_{Vt}\pi t}{L}\right),
\end{aligned} \tag{23}$$

which simply are the manufactured solutions, and the derivatives:

$$\begin{aligned}
\frac{\partial e_N^{\text{elec}}}{\partial x} &= \frac{(e_N^{\text{elec}})^2 a_{Tx} \pi T_{Vx} M_N}{LR T_V^2} \sin\left(\frac{a_{Tx}\pi x}{L}\right) - \frac{a_{Tx} \pi T_{Vx} R}{M_N L T_V^2} \sin\left(\frac{a_{Tx}\pi x}{L}\right) \text{AUX1}, \\
\frac{\partial e_{N_2}^{\text{elec}}}{\partial x} &= \frac{2(e_{N_2}^{\text{elec}})^2 a_{Tx} \pi T_{Vx} M_N}{LR T_V^2} \sin\left(\frac{a_{Tx}\pi x}{L}\right) - \frac{a_{Tx} \pi T_{Vx} R}{2M_N L T_V^2} \sin\left(\frac{a_{Tx}\pi x}{L}\right) \text{AUX2}, \\
\frac{\partial e_N^{\text{elec}}}{\partial t} &= -\frac{(e_N^{\text{elec}})^2 a_{Vt} \pi T_{Vt} M_N}{LR T_V^2} \cos\left(\frac{a_{Vt}\pi t}{L}\right) + \frac{a_{Vt} \pi T_{Vt} R}{M_N L T_V^2} \cos\left(\frac{a_{Vt}\pi t}{L}\right) \text{AUX1}, \\
\frac{\partial e_{N_2}^{\text{elec}}}{\partial t} &= -\frac{2(e_{N_2}^{\text{elec}})^2 a_{Vt} \pi T_{Vt} M_N}{LR T_V^2} \cos\left(\frac{a_{Vt}\pi t}{L}\right) + \frac{a_{Vt} \pi T_{Vt} R}{2M_N L T_V^2} \cos\left(\frac{a_{Vt}\pi t}{L}\right) \text{AUX2}, \\
\text{AUX1} &= \frac{\sum_{i=1}^{nel_N} (\theta_{N,i}^{\text{elec}})^2 g_{N,i} \exp(-\theta_{N,i}^{\text{elec}} / T_V)}{\sum_{i=1}^{nel_N} g_{N,i} \exp(-\theta_{N,i}^{\text{elec}} / T_V)}, \\
\text{AUX2} &= \frac{\sum_{i=1}^{nel_{N_2}} (\theta_{N_2,i}^{\text{elec}})^2 g_{N_2,i} \exp(-\theta_{N_2,i}^{\text{elec}} / T_V)}{\sum_{i=1}^{nel_{N_2}} g_{N_2,i} \exp(-\theta_{N_2,i}^{\text{elec}} / T_V)}.
\end{aligned} \tag{24}$$

2.2 Mass Conservation of Nitrogen Atom

The mass conservation equation for Nitrogen atom (N), written as an operator, is:

$$\mathcal{L} = \frac{\partial \rho_N}{\partial t} + \frac{\partial \rho_N u}{\partial x} - \dot{\omega}_N.$$

Analytically differentiating Equation (20) for ρ_N and u using operator \mathcal{L} defined above together with suitable substitution for $\dot{\omega}_N$ gives the source term Q_{ρ_N} :

$$\begin{aligned} Q_{\rho_N} = & -\frac{a_{\rho N t} \pi \rho_{N t}}{L} \sin\left(\frac{a_{\rho N t} \pi t}{L}\right) + \\ & + \frac{a_{\rho N x} \pi \rho_{N x} U}{L} \cos\left(\frac{a_{\rho N x} \pi x}{L}\right) + \frac{a_{u x} \pi u_x \text{Rho}_N}{L} \cos\left(\frac{a_{u x} \pi x}{L}\right) + \\ & - \dot{\omega}_N, \end{aligned}$$

with Rho_N and U defined in Equation (23). The source term $\dot{\omega}_N$ is given by:

$$\dot{\omega}_N = -2M_N \mathcal{R}_1$$

where M_N is the molar mass of Nitrogen and \mathcal{R}_1 is the reaction given according to Equation (12):

$$\mathcal{R}_1 = \frac{k_{f_1 N}}{K(T)} \frac{\text{Rho}_N^3}{M_N^3} - k_{f_1 N} \frac{\text{Rho}_{N_2} \text{Rho}_N}{2M_N^2} + \frac{k_{f_1 N_2}}{K(T)} \frac{\text{Rho}_N^2 \text{Rho}_{N_2}}{2M_N^3} - k_{f_1 N_2} \frac{\text{Rho}_{N_2}^2}{4M_N^2}, \quad (25)$$

$K(T)$ is a to-be-defined function for the equilibrium constant (13), and $k_{f_1 N}$ and $k_{f_1 N_2}$ are defined by:

$$\begin{aligned} k_{f_1 N} &= C_{f_1 N} \bar{T}^{\eta_{f_1 N}} \exp\left(\frac{-E_{aN}}{R\bar{T}}\right), \\ k_{f_1 N_2} &= C_{f_1 N_2} \bar{T}^{\eta_{f_1 N_2}} \exp\left(\frac{-E_{aN_2}}{R\bar{T}}\right), \\ \bar{T} &= T^q T_V^{1-q}. \end{aligned}$$

2.3 Mass Conservation of Nitrogen Molecule

The mass conservation equation for Nitrogen molecule (N_2), written as an operator, is:

$$\mathcal{L} = \frac{\partial \rho_{N_2}}{\partial t} + \frac{\partial \rho_{N_2} u}{\partial x} - \dot{\omega}_{N_2}.$$

Analytically differentiating Equation (20) for ρ_{N_2} and u using operator \mathcal{L} defined above together with suitable substitution for $\dot{\omega}_{N_2}$ gives the source term $Q_{\rho_{N_2}}$:

$$\begin{aligned} Q_{\rho_{N_2}} = & \frac{a_{\rho N_2 t} \pi \rho_{N_2 t}}{L} \cos\left(\frac{a_{\rho N_2 t} \pi t}{L}\right) + \\ & - \frac{a_{\rho N_2 x} \pi \rho_{N_2 x} U}{L} \sin\left(\frac{a_{\rho N_2 x} \pi x}{L}\right) + \frac{a_{u x} \pi u_x \text{Rho}_{N_2}}{L} \cos\left(\frac{a_{u x} \pi x}{L}\right) + \\ & - \dot{\omega}_{N_2}, \end{aligned}$$

where Rho_{N_2} and U defined in Equation (23) and:

$$\dot{\omega}_{N_2} = M_{N_2} \mathcal{R}_1 = 2M_N \mathcal{R}_1$$

with \mathcal{R}_1 given in Equation (25).

2.4 Momentum Conservation

For the generation of the analytical source term Q_u , x -momentum equation (3) is written as an operator \mathcal{L} :

$$\mathcal{L} = \frac{\partial \rho u}{\partial t} + \frac{\partial \rho u^2}{\partial x} + \frac{\partial p}{\partial x},$$

which, when operated in to Equations (20) and (21), provides source term Q_u :

$$\begin{aligned} Q_u = & -\frac{a_{ut}\pi u_t \text{Rho}}{L} \sin\left(\frac{a_{ut}\pi t}{L}\right) + \\ & + \frac{\pi \text{U}}{L} \left[-a_{\rho N_t} \rho_{N_t} \sin\left(\frac{a_{\rho N_t}\pi t}{L}\right) + a_{\rho N_2 t} \rho_{N_2 t} \cos\left(\frac{a_{\rho N_2 t}\pi t}{L}\right) \right] + \\ & + \frac{a_{\rho N_x} \pi \rho_{N_x} \text{U}^2}{L} \cos\left(\frac{a_{\rho N_x}\pi x}{L}\right) + \\ & - \frac{a_{\rho N_2 x} \pi \rho_{N_2 x} \text{U}^2}{L} \sin\left(\frac{a_{\rho N_2 x}\pi x}{L}\right) + \\ & + \frac{2a_{ux}\pi u_x \text{Rho} \text{U}}{L} \cos\left(\frac{a_{ux}\pi x}{L}\right) + \\ & - \frac{a_{T_x} \pi T_x R (2 \text{Rho}_N + \text{Rho}_{N_2}) \sin\left(\frac{a_{T_x}\pi x}{L}\right)}{2LM_N} + \\ & - \frac{\pi R \text{T}}{2LM_N} \left[-2a_{\rho N_x} \rho_{N_x} \cos\left(\frac{a_{\rho N_x}\pi x}{L}\right) + a_{\rho N_2 x} \rho_{N_2 x} \sin\left(\frac{a_{\rho N_2 x}\pi x}{L}\right) \right] \end{aligned} \quad (26)$$

with Rho , Rho_N , Rho_{N_2} , T and U defined in Equation (23).

2.5 Total Energy Conservation

The total energy equation is written as an operator:

$$\mathcal{L} = \frac{\partial \rho E}{\partial t} + \frac{\partial \rho u H}{\partial x},$$

where $H = E + \frac{p}{\rho}$ and $E = e^{\text{int}} + \frac{u^2}{2}$, with p and e^{int} as defined in Equations (11) and (6), respectively.

Source term Q_E is obtained by operating \mathcal{L} on Equations (20) and (21):

$$\begin{aligned} Q_E = & -\frac{a_{ut}\pi u_t \text{Rho} \text{U}}{L} \sin\left(\frac{a_{ut}\pi t}{L}\right) + \\ & - \frac{(6 \text{Rho}_N + 5 \text{Rho}_{N_2}) a_{T_t} \pi T_t R}{4LM_N} \sin\left(\frac{a_{T_t}\pi t}{L}\right) + \\ & - \frac{(h_N^0 + e_N^{\text{elec}}) a_{\rho N_t} \pi \rho_{N_t}}{L} \sin\left(\frac{a_{\rho N_t}\pi t}{L}\right) + \\ & + \frac{(h_{N_2}^0 + e_{N_2}^{\text{vib}} + e_{N_2}^{\text{elec}}) a_{\rho N_2 t} \pi \rho_{N_2 t}}{L} \cos\left(\frac{a_{\rho N_2 t}\pi t}{L}\right) + \\ & - \frac{\pi R \text{T}}{4LM_N} \left[6a_{\rho N_t} \rho_{N_t} \sin\left(\frac{a_{\rho N_t}\pi t}{L}\right) - 5a_{\rho N_2 t} \rho_{N_2 t} \cos\left(\frac{a_{\rho N_2 t}\pi t}{L}\right) \right] + \\ & + \frac{\pi \text{U}^2}{2L} \left[-a_{\rho N_t} \rho_{N_t} \sin\left(\frac{a_{\rho N_t}\pi t}{L}\right) + a_{\rho N_2 t} \rho_{N_2 t} \cos\left(\frac{a_{\rho N_2 t}\pi t}{L}\right) \right] + \\ & + \frac{e_{N_2}^{\text{vib}} (\theta_{N_2}^{\text{vib}} R + 2M_N e_{N_2}^{\text{vib}}) a_{T_v t} \pi T_v \text{Rho}_{N_2}}{LR \text{T}_v^2} \cos\left(\frac{a_{T_v t}\pi t}{L}\right) + \\ & + \frac{\partial e_N^{\text{elec}}}{\partial t} \text{Rho}_N + \frac{\partial e_{N_2}^{\text{elec}}}{\partial t} \text{Rho}_{N_2} + \\ & + \dots \end{aligned} \quad (27)$$

$$\begin{aligned}
& + \frac{3a_{ux}\pi u_x \text{Rho} \text{U}^2}{2L} \cos\left(\frac{a_{ux}\pi x}{L}\right) + \\
& + \frac{(h_{\text{N}}^0 + e_{\text{N}}^{\text{elec}})a_{\rho \text{N}x}\pi \rho_{\text{N}x} \text{U}}{L} \cos\left(\frac{a_{\rho \text{N}x}\pi x}{L}\right) + \\
& - \frac{(h_{\text{N}_2}^0 + e_{\text{N}_2}^{\text{elec}} + e_{\text{N}_2}^{\text{vib}})a_{\rho \text{N}_2x}\pi \rho_{\text{N}_2x} \text{U}}{L} \sin\left(\frac{a_{\rho \text{N}_2x}\pi x}{L}\right) + \\
& + \frac{(10 \text{Rho}_{\text{N}} + 7 \text{Rho}_{\text{N}_2})a_{ux}\pi u_x R \text{T}}{4LM_{\text{N}}} \cos\left(\frac{a_{ux}\pi x}{L}\right) + \\
& + \frac{(h_{\text{N}}^0 + e_{\text{N}}^{\text{elec}})a_{ux}\pi u_x \text{Rho}_{\text{N}}}{L} \cos\left(\frac{a_{ux}\pi x}{L}\right) + \\
& + \frac{(h_{\text{N}_2}^0 + e_{\text{N}_2}^{\text{elec}} + e_{\text{N}_2}^{\text{vib}})a_{ux}\pi u_x \text{Rho}_{\text{N}_2}}{L} \cos\left(\frac{a_{ux}\pi x}{L}\right) + \\
& - \frac{(10 \text{Rho}_{\text{N}} + 7 \text{Rho}_{\text{N}_2})a_{T_x}\pi T_x R \text{U}}{4LM_{\text{N}}} \sin\left(\frac{a_{T_x}\pi x}{L}\right) + \\
& - \frac{e_{\text{N}_2}^{\text{vib}} \theta_{\text{N}_2}^{\text{vib}} a_{T_Vx}\pi T_{Vx} \text{Rho}_{\text{N}_2} \text{U}}{L \text{T}_V^2} \sin\left(\frac{a_{T_Vx}\pi x}{L}\right) + \\
& - \frac{2(e_{\text{N}_2}^{\text{vib}})^2 a_{T_Vx}\pi T_{Vx} M_{\text{N}} \text{Rho}_{\text{N}_2} \text{U}}{L R \text{T}_V^2} \sin\left(\frac{a_{T_Vx}\pi x}{L}\right) + \\
& - \frac{\pi \text{U}^3}{2L} \left[-a_{\rho \text{N}x} \rho_{\text{N}x} \cos\left(\frac{a_{\rho \text{N}x}\pi x}{L}\right) + a_{\rho \text{N}_2x} \rho_{\text{N}_2x} \sin\left(\frac{a_{\rho \text{N}_2x}\pi x}{L}\right) \right] + \\
& - \frac{\pi R \text{U} \text{T}}{4LM_{\text{N}}} \left[-10a_{\rho \text{N}x} \rho_{\text{N}x} \cos\left(\frac{a_{\rho \text{N}x}\pi x}{L}\right) + 7a_{\rho \text{N}_2x} \rho_{\text{N}_2x} \sin\left(\frac{a_{\rho \text{N}_2x}\pi x}{L}\right) \right] + \\
& + \frac{\partial e_{\text{N}}^{\text{elec}}}{\partial x} \text{Rho}_{\text{N}} \text{U} + \frac{\partial e_{\text{N}_2}^{\text{elec}}}{\partial x} \text{Rho}_{\text{N}_2} \text{U}
\end{aligned} \tag{28}$$

where Rho , Rho_{N} , Rho_{N_2} , T and U are given in Equation (23), the derivatives $\frac{\partial e_{\text{N}}^{\text{elec}}}{\partial x}$, $\frac{\partial e_{\text{N}_2}^{\text{elec}}}{\partial x}$, $\frac{\partial e_{\text{N}}^{\text{elec}}}{\partial t}$ and $\frac{\partial e_{\text{N}_2}^{\text{elec}}}{\partial t}$ are given in Equation (24), and:

$$\begin{aligned}
e_{\text{N}}^{\text{elec}} &= \frac{R}{M_{\text{N}}} \frac{\sum_{i=1}^{nel_{\text{N}}} \theta_{\text{N},i}^{\text{elec}} g_{\text{N},i} \exp(-\theta_{\text{N},i}^{\text{elec}} / \text{T}_V)}{\sum_{i=1}^{nel_{\text{N}}} g_{\text{N},i} \exp(-\theta_{\text{N},i}^{\text{elec}} / \text{T}_V)}, \\
e_{\text{N}_2}^{\text{elec}} &= \frac{R}{2M_{\text{N}}} \frac{\sum_{i=1}^{nel_{\text{N}_2}} \theta_{\text{N}_2,i}^{\text{elec}} g_{\text{N}_2,i} \exp(-\theta_{\text{N}_2,i}^{\text{elec}} / \text{T}_V)}{\sum_{i=1}^{nel_{\text{N}_2}} g_{\text{N}_2,i} \exp(-\theta_{\text{N}_2,i}^{\text{elec}} / \text{T}_V)}, \\
e_{\text{N}_2}^{\text{vib}} &= \frac{R}{2M_{\text{N}}} \frac{\theta_{\text{N}_2}^{\text{vib}}}{\exp(\theta_{\text{N}_2}^{\text{vib}} / \text{T}_V) - 1}.
\end{aligned} \tag{29}$$

2.6 Vibrational Energy Conservation

The vibrational energy equation is written as an operator:

$$\mathcal{L} = \frac{\partial \rho e_V}{\partial t} + \frac{\partial e_V \rho u}{\partial x} - \dot{\omega}_V,$$

For the N-N₂ mixture, e_V is given by Equation (10):

$$e_V = \frac{\rho_{\text{N}_2}}{\rho} e_{\text{N}_2}^{\text{vib}} + \frac{\rho_{\text{N}}}{\rho} e_{\text{N}}^{\text{elec}} + \frac{\rho_{\text{N}_2}}{\rho} e_{\text{N}_2}^{\text{elec}}.$$

Therefore, source term Q_{e_V} is obtained by operating \mathcal{L} on Equations (20) and (21):

$$\begin{aligned}
Q_{e_V} = & -\frac{e_N^{\text{elec}} a_{\rho N t} \pi \rho_{N t}}{L} \sin\left(\frac{a_{\rho N t} \pi t}{L}\right) + \\
& + \frac{(e_{N_2}^{\text{vib}} + e_{N_2}^{\text{elec}}) a_{\rho N_2 t} \pi \rho_{N_2 t}}{L} \cos\left(\frac{a_{\rho N_2 t} \pi t}{L}\right) + \\
& + \frac{e_{N_2}^{\text{vib}} (\theta_{N_2}^{\text{vib}} R + 2 M_N e_{N_2}^{\text{vib}}) a_{T_V t} \pi T_V t \text{Rho}_{N_2}}{L R T_V^2} \cos\left(\frac{a_{T_V t} \pi t}{L}\right) + \\
& + \frac{\partial e_N^{\text{elec}}}{\partial t} \text{Rho}_N + \frac{\partial e_{N_2}^{\text{elec}}}{\partial t} \text{Rho}_{N_2} + \\
& + \frac{e_N^{\text{elec}} a_{\rho N x} \pi \rho_{N x} U}{L} \cos\left(\frac{a_{\rho N x} \pi x}{L}\right) + \\
& - \frac{(e_{N_2}^{\text{elec}} + e_{N_2}^{\text{vib}}) a_{\rho N_2 x} \pi \rho_{N_2 x} U}{L} \sin\left(\frac{a_{\rho N_2 x} \pi x}{L}\right) + \\
& + \frac{e_N^{\text{elec}} a_{u x} \pi u_x \text{Rho}_N}{L} \cos\left(\frac{a_{u x} \pi x}{L}\right) + \\
& + \frac{(e_{N_2}^{\text{elec}} + e_{N_2}^{\text{vib}}) a_{u x} \pi u_x \text{Rho}_{N_2}}{L} \cos\left(\frac{a_{u x} \pi x}{L}\right) + \\
& - \frac{e_{N_2}^{\text{vib}} \theta_{N_2}^{\text{vib}} a_{T_V x} \pi T_V x \text{Rho}_{N_2} U}{L T_V^2} \sin\left(\frac{a_{T_V x} \pi x}{L}\right) + \\
& - \frac{2(e_{N_2}^{\text{vib}})^2 a_{T_V x} \pi T_V x M_N \text{Rho}_{N_2} U}{L R T_V^2} \sin\left(\frac{a_{T_V x} \pi x}{L}\right) + \\
& + \frac{\partial e_N^{\text{elec}}}{\partial x} \text{Rho}_N U + \frac{\partial e_{N_2}^{\text{elec}}}{\partial x} \text{Rho}_{N_2} U + \\
& - \dot{\omega}_V
\end{aligned} \tag{30}$$

where Rho_N , Rho_{N_2} , T and U are given in Equation (23), e_N^{elec} , $e_{N_2}^{\text{elec}}$ and $e_{N_2}^{\text{vib}}$ are given in Equation (29). Source term $\dot{\omega}_V$ is given according to Section 1.2 as:

$$\dot{\omega}_V = \dot{\omega}_N e_N^{\text{elec}} + \dot{\omega}_{N_2} (e_{N_2}^{\text{vib}} + e_{N_2}^{\text{elec}}) + \text{Rho}_{N_2} (e_{N_2,eq}^{\text{vib}} - e_{N_2}^{\text{vib}}) \left[\frac{2 \text{Rho}_N}{(2 \text{Rho}_N + \text{Rho}_{N_2}) \tau_{N_2 N}^{\text{vib}}} + \frac{\text{Rho}_{N_2}}{(2 \text{Rho}_N + \text{Rho}_{N_2}) \tau_{N_2 N_2}^{\text{vib}}} \right],$$

with

$$\begin{aligned}
e_{N_2,eq}^{\text{vib}} &= \frac{R}{2 M_N \exp(\theta_{N_2}^{\text{vib}} / T) - 1}, \\
\tau_{N_2 N_2}^{\text{vib}} &= \frac{\exp\left(\frac{29}{25000} M_N^{1/2} (\theta_{N_2}^{\text{vib}})^{4/3} \left[T^{-1/3} - \frac{3}{2000} M_N^{1/4}\right] - 18.42\right)}{P}, \\
\tau_{N_2 N}^{\text{vib}} &= \frac{\exp\left(\frac{29}{75000} (6 M_N)^{1/2} (\theta_{N_2}^{\text{vib}})^{4/3} \left[T^{-1/3} - \frac{1}{200} (54 M_N)^{1/4}\right] - 18.42\right)}{P}.
\end{aligned} \tag{31}$$

and P is given by the Dalton's law (11):

$$P = \frac{\text{Rho}_N T R}{M_N} + \frac{\text{Rho}_{N_2} T R}{2 M_N}.$$

3 Hierarchic MMS

The complexity, and consequently length, of the source terms increase with both dimension and physics handled by the governing equations. In some cases, such as the vibration energy equation, the final expression for Q_{e_V} may pass 7 million characters, including parenthesis and mathematical operators, prior to factorization.

Applying commands in order to simplify such extensive expression is challenging even with a very good machine; thus, a suitable alternative to this issue is to simplify the equation by dividing it into a combination of sub-operators handling different physical phenomena. Then, each one of the operators may be applied to the manufactured solutions individually and the resulting source terms are combined back to represent the source term for the original equation.

For instance, instead of writing the 1D vibrational energy equation using one single operator \mathcal{L} :

$$\mathcal{L} = \frac{\partial \rho e_V}{\partial t} + \frac{\partial e_V \rho u}{\partial x} - \dot{\omega}_V, \quad (32)$$

to then be used in the MMS, let equation (32) be written in three distinct operators:

$$\begin{aligned} \mathcal{L}_1 &= \frac{\partial \rho e_V}{\partial t}, \\ \mathcal{L}_2 &= \frac{\partial e_V \rho u}{\partial x}, \\ \mathcal{L}_3 &= -\dot{\omega}_V. \end{aligned}$$

After the application of \mathcal{L}_1 , \mathcal{L}_2 and \mathcal{L}_3 , the corresponding sub-source terms are also simplified, factorized and sorted. Then, the final factorized version is checked against the original one, to assure that not human error has been introduced. This strategy allowed the original 7,753,932 character-long expression for Q_{e_V} to be reduced to less than 11,500. Furthermore, this strategy combined with the use of the auxiliary variables listed in Equations (23) and (24) allows the original source term to be reduced to only 3,200 characters (illustrated in Equation 30).

3.1 Boundary Conditions and C Codes

Source terms Q_{ρ_N} , $Q_{\rho_{N_2}}$, Q_u , Q_E and Q_{e_V} have been generated by replacing the analytical Expressions (20) and (21) into respective Equations (1)–(5), followed by the usage of Maple commands for collecting, sorting and factorizing the terms, using the strategy discussed above. Files containing C codes for the source terms have also been generated. They are: `Euler_1d_transient_chemistry_2T_rho_N_code.C`, `Euler_1d_transient_chemistry_2T_rho_N2_code.C`, `Euler_1d_transient_chemistry_2T_u_code.C`, `Euler_1d_transient_chemistry_2T_E_code.C` and `Euler_1d_transient_chemistry_2T_eV_code.C`.

An example of the automatically generated C file from the source term for the mass conservation equation of N_2 is:

```
#include <math.h>

double SourceQ_rho_N2 (double x, double t)
{
    double Q_rho_N2;
    double RHO_N;
    double RHO_N2;
    double U;
    double T;
    double TV;
    double kf1_N;
    double kf1_N2;
    double K;
    double R1;
    double w_dot_N2;
    double T_bar;
    RHO_N = rho_N_0 + rho_N_x * sin(a_rho_N_x * PI * x / L) + rho_N_t * cos(a_rho_N_t * PI * t / L);
    RHO_N2 = rho_N2_0 + rho_N2_x * cos(a_rho_N2_x * PI * x / L) + rho_N2_t * sin(a_rho_N2_t * PI * t / L);
    U = u_0 + u_x * sin(a_u_x * PI * x / L) + u_t * cos(a_u_t * PI * t / L);
    T = T_0 + T_x * cos(a_Tx * PI * x / L) + T_t * cos(a_Tt * PI * t / L);
    TV = Tv_0 + Tv_x * cos(a_Tvx * PI * x / L) + Tv_t * sin(a_Tvt * PI * t / L);
    T_bar = pow(T, q) * pow(TV, 0.1e1 - q);
    K = calculate_equilibrium_constant_K(T);
    kf1_N2 = Cf1_N2 * pow(T_bar, etaf1_N2) * exp(-Ea_N2 / R / T_bar);
    kf1_N = Cf1_N * pow(T_bar, etaf1_N) * exp(-Ea_N / R / T_bar);
    R1 = kf1_N * pow(RHO_N, 0.3e1) / K * pow(M_N, -0.3e1) - kf1_N * RHO_N2 * RHO_N * pow(M_N, -0.2e1) / 0.2e1
        + kf1_N2 * RHO_N * RHO_N * RHO_N2 / K * pow(M_N, -0.3e1) / 0.2e1 - kf1_N2 * RHO_N2 * RHO_N2 * pow(M_N, -0.2e1) / 0.4e1;
    w_dot_N2 = 0.2e1 * M_N * R1;
    Q_rho_N2 = -a_rho_N2_x * PI * rho_N2_x * U * sin(a_rho_N2_x * PI * x / L) / L
        + a_u_x * PI * u_x * RHO_N2 * cos(a_u_x * PI * x / L) / L
```

```

    + a_rho_N2_t * PI * rho_N2_t * cos(a_rho_N2_t * PI * t / L) / L
    - w_dot_N2;
return(Q_rho_N2);
}

```

and the source term for the total energy E of the mixture is:

```

#include <math.h>

double SourceQ_E (double x, double t, int energy_level_N, int energy_level_N2, double *g_N, double *g_N2, double *theta_e_N,
double *theta_e_N2)
{
    double Q_E;
    double e_elec_N;
    double e_elec_N_num;
    double e_elec_N_den;
    double e_elec_N2;
    double e_elec_N2_num;
    double e_elec_N2_den;
    double e_vib_N2;
    double RHO;
    double RHO_N;
    double RHO_N2;
    double U;
    double T;
    double TV;
    double P;
    double De_elecN2_Dx;
    double De_elecN_Dx;
    double AUX1;
    double AUX2;
    int i;
    double De_elecN2_Dt;
    double De_elecN_Dt;
    RHO_N = rho_N_0 + rho_N_x * sin(a_rho_N_x * PI * x / L) + rho_N_t * cos(a_rho_N_t * PI * t / L);
    RHO_N2 = rho_N2_0 + rho_N2_x * cos(a_rho_N2_x * PI * x / L) + rho_N2_t * sin(a_rho_N2_t * PI * t / L);
    RHO = RHO_N + RHO_N2;
    U = u_0 + u_x * sin(a_ux * PI * x / L) + u_t * cos(a_ut * PI * t / L);
    T = T_0 + T_x * cos(a_Tx * PI * x / L) + T_t * cos(a_Tt * PI * t / L);
    TV = Tv_0 + Tv_x * cos(a_Tvx * PI * x / L) + Tv_t * sin(a_Tvt * PI * t / L);
    P = RHO_N * R_N * T + RHO_N2 * R_N2 * T;
    e_elec_N_num = 0.0e0;
    e_elec_N2_num = 0.0e0;
    e_elec_N_den = g_N_0;
    e_elec_N2_den = g_N2_0;
    for (i = 1; i <= energy_level_N; i++)
    {
        e_elec_N_den = e_elec_N_den + g_N[i - 1] * exp(-theta_e_N[i - 1] / TV);
        e_elec_N_num = e_elec_N_num + theta_e_N[i - 1] * g_N[i - 1] * exp(-theta_e_N[i - 1] / TV);
        AUX1 = AUX1 + pow(theta_e_N[i - 1], 0.2e1) * g_N[i - 1] * exp(-theta_e_N[i - 1] / TV);
    }
    for (i = 1; i <= energy_level_N2; i++)
    {
        e_elec_N2_den = e_elec_N2_den + g_N2[i - 1] * exp(-theta_e_N2[i - 1] / TV);
        e_elec_N2_num = e_elec_N2_num + theta_e_N2[i - 1] * g_N2[i - 1] * exp(-theta_e_N2[i - 1] / TV);
        AUX2 = AUX2 + pow(theta_e_N2[i - 1], 0.2e1) * g_N2[i - 1] * exp(-theta_e_N2[i - 1] / TV);
    }
    e_elec_N = R * e_elec_N_num / M_N / e_elec_N_den;
    e_elec_N2 = R * e_elec_N2_num / M_N / e_elec_N2_den / 0.2e1;
    e_vib_N2 = theta_v_N2 * R / M_N / (exp(theta_v_N2 / TV) - 0.1e1) / 0.2e1;
    De_elecN_Dx = e_elec_N * e_elec_N * M_N * a_Tvx * PI * Tv_x * sin(a_Tvx * PI * x / L) / R * pow(TV, -0.2e1) / L
    - R * AUX1 * a_Tvx * PI * Tv_x * sin(a_Tvx * PI * x / L) / M_N / e_elec_N_den * pow(TV, -0.2e1) / L;
    De_elecN2_Dx = 0.2e1 * e_elec_N2 * e_elec_N2 * M_N * a_Tvx * PI * Tv_x * sin(a_Tvx * PI * x / L) / R * pow(TV, -0.2e1) / L
    - R * AUX2 * a_Tvx * PI * Tv_x * sin(a_Tvx * PI * x / L) / M_N / e_elec_N2_den * pow(TV, -0.2e1) / L / 0.2e1;
    De_elecN_Dt = -e_elec_N * e_elec_N * a_Tvt * PI * Tv_t * M_N * cos(a_Tvt * PI * t / L) / R * pow(TV, -0.2e1) / L
    + a_Tvt * PI * Tv_t * R * AUX1 * cos(a_Tvt * PI * t / L) / M_N / e_elec_N_den * pow(TV, -0.2e1) / L;
    De_elecN2_Dt = -0.2e1 * e_elec_N2 * e_elec_N2 * a_Tvt * PI * Tv_t * M_N * cos(a_Tvt * PI * t / L) / R * pow(TV, -0.2e1) / L
    + a_Tvt * PI * Tv_t * R * AUX2 * cos(a_Tvt * PI * t / L) / M_N / e_elec_N2_den * pow(TV, -0.2e1) / L / 0.2e1;
    Q_E = 0.3e1 / 0.2e1 * a_ux * PI * u_x * RHO * U * U * cos(a_ux * PI * x / L) / L
    - (0.10e2 * RHO_N + 0.7e1 * RHO_N2) * a_Tx * PI * T_x * R * U * sin(a_Tx * PI * x / L) / M_N / L / 0.4e1
    + (0.10e2 * RHO_N + 0.7e1 * RHO_N2) * a_ux * PI * u_x * R * T * cos(a_ux * PI * x / L) / M_N / L / 0.4e1
    - a_ut * PI * u_t * RHO * U * sin(a_ut * PI * t / L) / L
    + (h0_N + e_elec_N) * a_rho_N_x * PI * rho_N_x * U * cos(a_rho_N_x * PI * x / L) / L
    - (h0_N2 + e_vib_N2 + e_elec_N2) * a_rho_N2_x * PI * rho_N2_x * U * sin(a_rho_N2_x * PI * x / L) / L
    - (0.6e1 * RHO_N + 0.5e1 * RHO_N2) * a_Tt * PI * T_t * R * sin(a_Tt * PI * t / L) / M_N / L / 0.4e1
    - e_vib_N2 * a_Tvx * PI * Tv_x * theta_v_N2 * RHO_N2 * U * sin(a_Tvx * PI * x / L) / L * pow(TV, -0.2e1)
    + (h0_N + e_elec_N) * a_ux * PI * u_x * RHO_N * cos(a_ux * PI * x / L) / L
    + (h0_N2 + e_vib_N2 + e_elec_N2) * a_ux * PI * u_x * RHO_N2 * cos(a_ux * PI * x / L) / L
    - (h0_N + e_elec_N) * a_rho_N_t * PI * rho_N_t * sin(a_rho_N_t * PI * t / L) / L
    + (h0_N2 + e_vib_N2 + e_elec_N2) * a_rho_N2_t * PI * rho_N2_t * cos(a_rho_N2_t * PI * t / L) / L
}

```

```

- (-0.10e2 * a_rho_N_x * rho_N_x * cos(a_rho_N_x * PI * x / L) + 0.7e1 * a_rho_N2_x * rho_N2_x * sin(a_rho_N2_x * PI * x / L))
  * PI * R * U * T / M_N / L / 0.4e1 - (-a_rho_N_x * rho_N_x * cos(a_rho_N_x * PI * x / L)
+ a_rho_N2_x * rho_N2_x * sin(a_rho_N2_x * PI * x / L)) * PI * pow(U, 0.3e1) / L / 0.2e1
- 0.2e1 * M_N * e_vib_N2 * e_vib_N2 * a_Tvx * PI * Tv_x * RH0_N2 * U * sin(a_Tvx * PI * x / L) / R * pow(TV, -0.2e1) / L
- (0.6e1 * a_rho_N_t * rho_N_t * sin(a_rho_N_t * PI * t / L) - 0.5e1 * a_rho_N2_t * rho_N2_t * cos(a_rho_N2_t * PI * t / L))
  * PI * R * T / M_N / L / 0.4e1 + (-a_rho_N_t * rho_N_t * sin(a_rho_N_t * PI * t / L)
+ a_rho_N2_t * rho_N2_t * cos(a_rho_N2_t * PI * t / L)) * PI * U * U / L / 0.2e1
+ e_vib_N2 * (theta_v_N2 * R + 0.2e1 * M_N * e_vib_N2) * a_Tvt * PI * Tv_t * RH0_N2 * cos(a_Tvt * PI * t / L) / R * pow(TV, -0.2e1) / L
+ De_elecN_Dx * RH0_N * U + De_elecN2_Dx * RH0_N2 * U + De_elecN_Dt * RH0_N + De_elecN2_Dt * RH0_N2;
return(Q_E);
}

```

Finally, the gradients of the analytical solutions (20) and (21) have also been computed and their respective C codes are presented in `Euler_1d.chemistry_manuf_solutions_grad_and_code.C`. Therefore,

$$\begin{aligned}
\nabla \rho_N &= \frac{a_{\rho N x} \pi \rho_{N x}}{L} \cos\left(\frac{a_{\rho N x} \pi x}{L}\right), & \nabla \rho_{N_2} &= \frac{a_{\rho N_2 x} \pi \rho_{N_2 x}}{L} \sin\left(\frac{a_{\rho N_2 x} \pi x}{L}\right), \\
\nabla T &= -\frac{a_{T x} \pi T_x}{L} \sin\left(\frac{a_{T x} \pi x}{L}\right), & \nabla u &= \frac{a_{u x} \pi u_x}{L} \cos\left(\frac{a_{u x} \pi x}{L}\right), \\
\nabla T_V &= -\frac{a_{T_V x} \pi T_{V x}}{L} \sin\left(\frac{a_{T_V x} \pi x}{L}\right), & \nabla \rho &= \nabla(\rho_N) + \nabla(\rho_{N_2}),
\end{aligned} \tag{33}$$

are written in C language as:

```

grad_rho_an_N[0] = rho_N_x * cos(a_rho_N_x * pi * x / L) * a_rho_N_x * pi / L;
grad_rho_an_N2[0] = -rho_N2_x * sin(a_rho_N2_x * pi * x / L) * a_rho_N2_x * pi / L;
grad_rho_an[0] = rho_N_x * cos(a_rho_N_x * pi * x / L) * a_rho_N_x * pi / L
  - rho_N2_x * sin(a_rho_N2_x * pi * x / L) * a_rho_N2_x * pi / L;
grad_u_an[0] = u_x * cos(a_u_x * pi * x / L) * a_u_x * pi / L;
grad_T_an[0] = -T_x * sin(a_T_x * pi * x / L) * a_T_x * pi / L;
grad_Tv_an[0] = -Tv_x * sin(a_Tv_x * pi * x / L) * a_Tv_x * pi / L;

```

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A List of model / manufactured solution parameters

There are a variety of parameters present in the thermochemical nonequilibrium flow of a inviscid fluid, due to both fluid properties and the constants arising from the chosen manufactured solutions.

Fluid properties: $R, M_N, h_N^0, h_{N_2}^0, \theta_{N_2}^{\text{vib}}, \theta_N^{\text{elec}}, \theta_{N_2}^{\text{elec}}, g_N, g_{N_2}, nel_N, nel_{N_2}, C_{f1N}, \eta_{f1N}, E_{aN}, C_{f1N_2}, \eta_{f1N_2}, E_{aN_2}$ and q , where $\theta_{N_2}^{\text{elec}}, \theta_N^{\text{elec}}, g_N, g_{N_2}$ are lists of values and their size is either n_{elN} or n_{elN_2} , depending on the species N or N_2 .

In the C codes, these values are represented, respectively, by:

R, M_N, h0_N, h0_N2, theta_v_N2, theta_e_N, theta_e_N2, g_N, g_N2, energy_level_N, energy_level_N2, Cf1_N, etaf1_N, Ea_N, Cf1_N2, etaf1_N2, Ea_N2, q.

Manufactured solutions: $\rho_{N0}, \rho_{Nx}, \rho_{Nt}, a_{\rho Nx}, a_{\rho Nt}, \rho_{N_20}, \rho_{N_2x}, \rho_{N_2t}, a_{\rho N_2x}, a_{\rho N_2t}, u_0, u_x, u_t, a_{ux}, a_{ut}, T_0, T_x, T_t, a_{Tx}, a_{Tt}, T_{V0}, T_{Vx}, a_{TVx}, a_{TVt}, L$.

In the C codes, these values are represented, respectively, by:

rho_N_0, rho_N_x, rho_N_t, a_rho_N_x, a_rho_N_t, rho_N2_0, rho_N2_x, rho_N2_t, a_rho_N2_x, a_rho_N2_t, u_0, u_x, u_t, a_ux, a_ut, T_0, T_x, T_t, a_Tx, a_Tt, Tv_0, Tv_x, Tv_t, a_Tvx, a_Tvt, L.

Examples of data values: The data for each of the species are given in Table 1: M_s is the species molar mass, R_s is the species gas constant, h_s^0 is the activation energy, and θ_s^{vib} is the species characteristic temperature of vibration for the 5-species model (Kessler and Awruch, 2004).

Table 1: Parameters for Nitrogen atom and molecule.

	N ₂	N
M_s [kg/kg-mol]	28.02	14.01
R_s [J/ kg K]	296.7	593.6
h_s^0 [K]	0	33.59×10^6
θ_s^{vib} [K]	3393	-

Moreover, the characteristic electronic temperature θ_s^{elec} , degeneracy of the electronic mode g_s and total number of electronic levels nel_s of Nitrogen atom and molecule are presented in Table 2 (Kirk et al., 2009).

Table 2: Electronic data of N and N₂

Species s	nel_s	θ_s^{elec} [K]	g_s
N	3	0	4
		2.76647×10^4	10
		4.14931×10^4	6
N ₂	15	0	1
		7.22316×10^4	3
		8.57786×10^4	6
		8.60503×10^4	6
		9.53512×10^4	3
		9.80564×10^4	1
		9.96827×10^4	2
		1.04898×10^5	2
		1.11649×10^5	5
		1.22584×10^5	1
		1.24886×10^5	6
		1.28248×10^5	6
		1.33806×10^5	10
		1.40430×10^5	6
		1.50496×10^5	6